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CO_2 Balance in a Compression and Purification Unit (CPU)

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Abstract

The next step for many CO_2 capture technologies is to move to commercial scale [1]. Without the experience that can only be gained through pilot plants, CCS will not become a commercially viable proposition due to unresolved technical challenges and uncertain cost estimations. Individual demonstration projects need to be at a scale that is sufficiently large to be representative of commercial operation.
One of these individual projects was carried out by *Fundación Ciudad de la Energía* (CIUDEN), who successfully completed the full CO_2 capture process in its Technology Development Centre for CO_2 Capture and Transport using oxycombustion in Circulating Fluidized Bed (CFB) boiler and a cryogenic CO_2 Compression and Purification Unit (CPU).

Focused on the CIUDEN´s CPU, this paper describes the unit designed by Air Liquide, their sub-units in which the CO_2 composition is increased to achieve the design value of >99.0 % v in the liquefied product stream and a final case study based on an empirical mass balance; considering this data, in addition to the CO_2 purity, a mass balance provides the recovery rate value; this last parameter was lower than the expected value. Studying the specific behaviour of each subunit, it is concluded that the warm-part of the CPU presents a recovery rate higher than 99 % whereas the cold part of the unit (expansion and distillation columns to remove NO_x and incondensable gases) obtained an average value of 60 %, generated mainly because the CO_2 composition in the inlet of the CPU was lower than 70 % v w/b (design value). This was due to higher N_2 content in the flue gas.

Considering these results, the conclusions are very clear that air infiltration must be minimised. It also demonstrates the necessity of increasing the quantity of operating hours on demonstration plants such as CIUDEN in order to further optimise the technology with the end goal of improving the business case for CCS.

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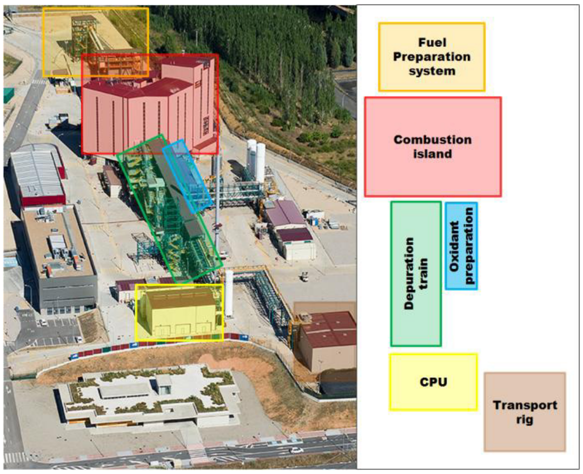
1. Introduction

The next step for many CO_2 capture technologies is to move to demonstration scale. Nevertheless, new technologies do not jump directly from the small scale to full-scale operation so demonstration on large pilots is therefore an interesting intermediate technical step with reduced risk exposure that facilitates learning-by-doing and culminates in a technology that can be sold in the marketplace

1.1. CIUDEN´s Centre

One of the European large scale projects was carried out by Foundation *Ciudad de la Energía* (CIUDEN). Firstly, worth mentioning is the layout of CIUDEN´s plant in order to have a clear idea about the size of the installations and, consequently, the representative results that could be obtained [2]. In general term, CIUDEN´s installation includes following main process units (see Fig. 1):



- Fuel preparation system, including a 15 t/h crusher and a 5 t/h ball mill. This process unit is designed to treat different fuels such as anthracite and petroleum coke (petcoke), among others.

- Combustion island: 20 MWth pulverized coal (PC) boiler and 30 MWth circulating fluidized bed (CFB) boiler. In particular, the present paper will be focus on the CFB boiler.

- Oxidant preparation system using steam. In CIUDEN´s plant, the sensible heat from flue gases is recovered using a liquid-gas heat exchanger (BFW HX) with boiler feed water (BFW) whereas the comburent preparation train uses steam to increase the oxidant streams temperatures.

Fig. 1 CIUDEN´s layout

- Combustion gases heat recovery system (BFW HX).

- Flue gas purification train that includes the multi-cyclones (not represented in the **¡Error! No se encuentra el origen de la referencia.**) prior to selective catalytic reactor (hereinafter, SCR) and bag filters to decrease the particulate concentration to less than 15 mg/Nm3. On the other hand, a system for collection, transport and

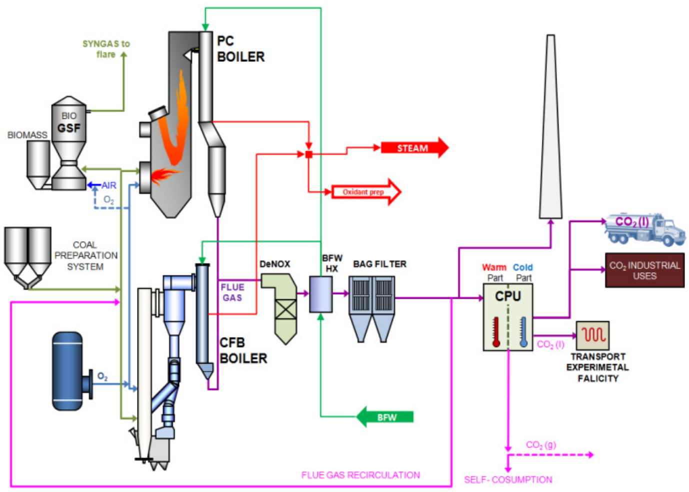


Fig. 2 Schematic process flow diagram

storage of solid residues and fly ashes is also included; regarding the solid residues, made-to-measure hermetic containers were designed for the bottom-ash in the CFB boiler as the residues are obtained at 300 ºC (after the refrigerated screw) whereas for the PC boiler, opened containers are used due to a wet rendler is installed to extract the bottom ashes.

- CO_2 compression and purification unit (see following chapter for details).
- CO_2 transport test rig including recirculation pump and heat exchanger systems in order to set operation pressures and temperatures within the range of 80 -110 barg and 10 - 30 ºC respectively. With the aim of operating the test rig in thermal conditions similar to those expected in CO_2 transport pipelines (mainly buried), the facility will be located inside a highly thermal isolated building with thermal control.
- Auxiliary service systems (oxygen, compressed air, LNG as auxiliary fuel, raw water, demineralised water, cooling water, CO_2 as inert fluid, etc.) necessary for the operation of the TDP.

1.2. CIUDEN´s CPU

The CPU is the unit in which the CO_2 is captured and purified from oxy-combustion flue gases. The plant size has been chosen to facilitate testing of technologies that will be “up-scalable” to the size required for a commercial plant while maintaining a reasonable cost and power consumption.

The unit can be thought of as comprising two different sections: the warm-part and the cold-part. The first part of the unit works at low pressure and was sized to treat the total flow of the flue gas coming from either PC or CFB boilers. This was done in order to have the possibility to test innovative flue gas scrubbing systems, filtration and drying at sufficiently large enough a size to allow extrapolation of the design at a commercial scale as a next step. In terms of equivalent “CO_2 capacity”, this part of the CPU could be rated as a ≈ 200 tpd.

The compression and cryogenic separation parts of the process were scaled down to produce 10 tpd CO_2 so as to reduce the overall investment cost of the plant. It is accepted that at commercial scale, centrifugal compressor technology will be used [3]. However, the size of the plant (≈ 300 acfm, @25 ºC, 1 barg) was not sufficient to make the implementation of this type of machines economical so reciprocating compressors were selected (see Fig. 3). Nevertheless even with this size the unit still demonstrates a capacity larger than the majority of the CO_2 capture pilot plants and, from the process point of view, the results obtained are representative of a commercial plant.

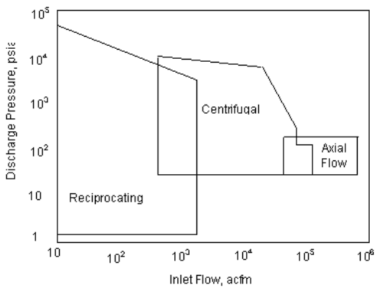


Fig. 3 Range chart for types of compressors

The CPU includes following functional process blocks [4]:

- Flue gas quench and acid gas scrubbing (at close to atmospheric pressure).
- High performance dust filter.
- Low pressure flue gas drying system.
- Compression of a flue gas partial stream (≈ 300 Nm^3/h).
- Cryogenic CO_2 separation, purification and CO_2 based refrigeration cycle.

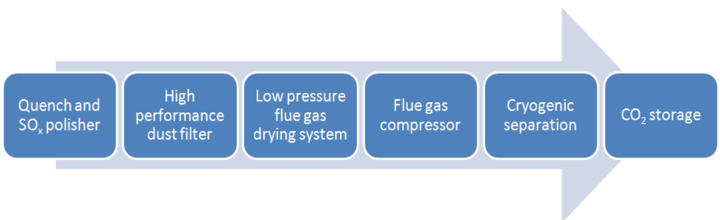


Fig. 4 CIUDEN´s CPU block diagram

The following section describes the main CPU sub-units:

- **Flue gas quench and acid gas scrubbing:** at the inlet of the CPU the flue gas temperature is in the range 150-200 ºC and the pressure is in the range -10 mbarg ÷ 10 mbarg. This gas is passed into a quench where it is cooled to at least the saturation temperature by direct contact with Na_2CO_3 aqueous dissolution. After this cooling stage, the gas will be scrubbed in a tower with the same solution in order to remove acidic compounds such as SOx, HCl and HF.

- **High performance dust filter:** After the quench and scrubbing tower, the flue gas is compressed to around 1,4 bara in the blower C111. It is then filtered down to a very low level of particulate matter load with a very high efficiency filtration system (F111). This very low dust load is required for reliable and efficient operation of the downstream process equipment.

- **Low pressure flue gas drying system:** a Temperature Swing Adsortion (TSA) unit located downstream of the high performance dust filtration system is responsible for drying the flue gas stream. The acid gas scrubbing upstream will protect the low pressure drying unit from potential problems caused by SOx. The first part of the drying system is a heat exchanger where water is condensed out by cooling first against cooling water and subsequently against chilled water. The second part of the drying system consist of three vessels (R371, R372 and R373) containing a specially selected adsorbent. While one vessel is used to adsorb water from the flue gas, the others will be regenerated.

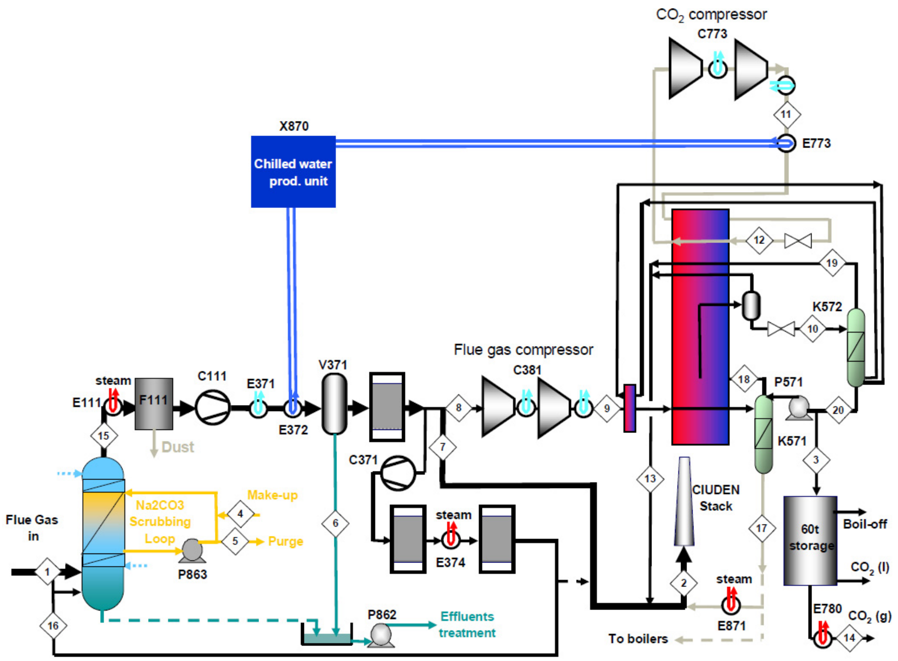


Fig. 5 CPU schematic process flow diagram

- **Flue gas compressor:** once the flue gas has been scrubbed, filtered and dried a portion (≈ 300 Nm3/h) is compressed in the flue gas compressor C381. The remaining flue gas is sent to the stack (stream 7 acoording toFig. 5). The flue gas is compressed to approximately 20 barg.

- **Cryogenic CO_2 separation and CO_2 based refrigeration cycle:** once the flue gas has been compressed, it is cooled to approximately -52 ºC in a brazed aluminium heat exchange (BAHX) to liquefy the CO_2. This temperature is chosen to be representative of the process that would be used on large scale commercial units. After this cooling, two distillation towers will remove NOx and incondensable gases (K571 adn K572 respectively); in the case of the first column, pure CO_2 from the product pressure vessel will be use to produce the liquid stream. The necessary cold for cooling the compressed flue gas to -52 ºC will be provided by a refrigeration cycle using pure CO_2 as the working fluid. This cycle include following steps (see Fig. 6): 1-2: condensation; 2-3: cooling down; 3-4: Joule Thomson expansion; 4-5: evaporation; 5-6 first stage compression; 6-7: second stage compression; 7-8: cooling down (compression heat removal) [5].

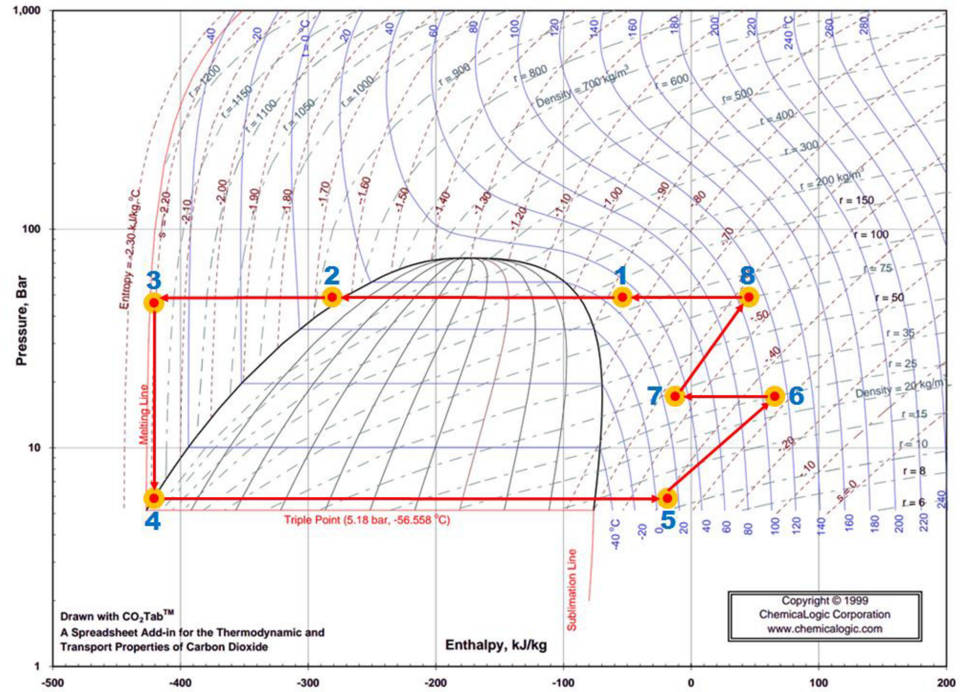


Fig. 6 Carbon Dioxide Pressure - Enthalpy diagram and cold cycle in the CPU

Nomenclature

BAHX	Brazed aluminium heat exchanger
BFW	Boiler feed water
CFB	Circulating fluidized bed
CPU	Compression and purification unit
HX	Heat exchanger
PC	Pulverized coal
SCR	Selective catalytic reactor
TSA	Temperature swing adsorption

2. Experimental procedure

Firstly, the coal used during the test campaign was anthracite from “El Bierzo”. Secondly, worth mentioning is the fact that, upstream of the CPU, the CFB boiler was in operation during this test campaign; downstream of the boiler, the reader is reminder that flue gases were treated in the cyclones and in the bag filter. After these units, the flue gases were fed to the CPU [6].

Once the CPU is achieved, it is clear that ineach subunit described in the chapter CIUDEN´s CPU, the CO_2 concentration is increased until the design values presented in the following table are achieved:

Table 1 Product stream design composition

Compound	Composition
CO_2	> 99 % v
SOx	< 100 ppm
NOx	< 100 ppm
H_2O	< 10 ppm
CO	< 2.000 ppm

In this paper following streams will be characterized using the CO_2 composition measured during a specific case study (see Fig. 4): streams #1, #15, #7, #8, #9, #18 and #3; for the first case (stream #1), an FTIR by GASMET was used whereas for the rest of the cases, a CO_2 analyzer by ABB was utilized.

Furthermore, the recovery rate will be calculated in accordance with Fig. 7 and equation (1) since, as previously explained, only ≈ 300 Nm^3/h are treated in the cold part of the unit, the rest of flue gases being vented to the atmosphere.

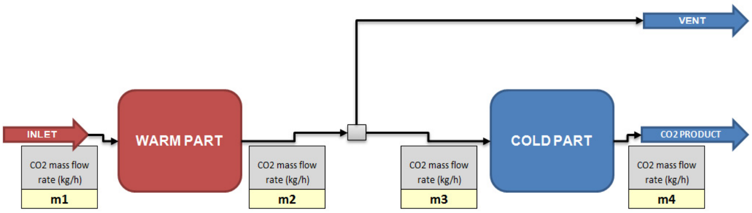


Fig. 7 Scheme for the recovery rate calculation

$$Global\ recovery\ rate\ = Recovery\ warm\ part \cdot Recovery\ cold\ part$$

$$Global\ recovery\ rate = \left(\frac{m_2}{m_1}\right) \cdot \left(\frac{m_4}{m_3}\right) = \left(\frac{m_{stream\ 8}}{m_{stream\ 1}}\right) \cdot \left(\frac{m_{stream\ 20}}{m_{stream\ 3}}\right) \quad (1)$$

3. Results and data analysis

3.1. Results

In the following tables, the mass balance main data are presented. These data were obtained during a specific test campaign (aprox. 8 hours of operation in which the stable period is selected) in which the CO_2 composition across the CPU was the main topic to be studied. Accordingly with the previous explanation of the unit, the results are divided between the warm part and the cold part of the CPU.

Table 2 Temperature and pressure of warm part streams

Variable	Stream #1	Stream #15	Stream #7	Stream #8
Temperature (ºC)	142	31	32	32
Pressure (mbarg)	3	-25	187	76

Table 3 Flow rate and compositions of warm part streams

Variable	Stream #1	Stream #15	Stream #7	Stream #8
Mass flow rate (kg/h)	6540	9241	5384	567
Compositions (% v w/b)				
CO_2	62,0300 (lower than CPU design value)	72,4367	75,7987	
H_20	18,1096	4,4356	0,0001	
N_2	15,2330	17,7766	18,6017	
Ar	0,3755	0,4381	0,4585	
SO_2	0,0419	0,0000	0,0000	
O_2	4,2017	4,9033	5,1309	
NO_x	0,0083	0,0096	0,0101	

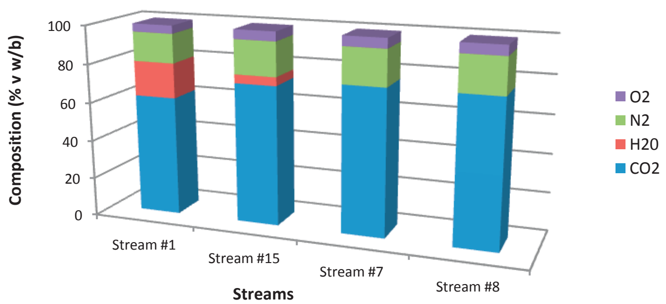


Fig. 8 CO_2 balance across the warm part of the CPU

Table 4 Temperature and pressure of cold part streams

Variable	Stream #9	Stream #18	Stream #3
Temperature (ºC)	29	-29	-34
Pressure (mbarg)	19,2	19,2	V-L Equilibrium

Table 5 Flow rate and compositions of cold part streams

Variable	Stream #9	Stream #18	Stream #3
Mass flow rate (kg/h)	567	635	266
Compositions (% v w/b)			
CO_2	75,7987	78,2200	98,9009
H_20	0,0001	0,0001	0,0000
N_2	18,6017	16,7466	0,0000
Ar	0,4585	0,4128	1,0623
SO_2	0,0000	0,0000	0,0000
O_2	5,1309	4,6192	0,0335
NO_x	0,0101	0,0013	0,0032

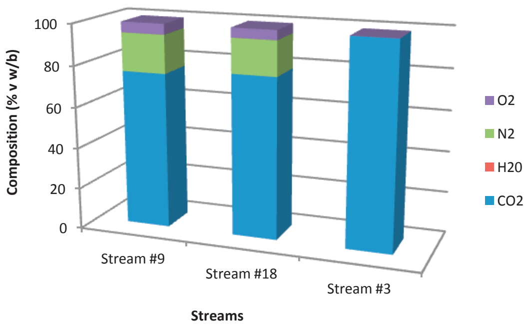


Fig. 9 CO_2 balance across the cold part of the CPU

3.2. Data analysis

Once the results have been presented, following table shows the recovery rates obtained for the warm part and for the cold part of the unit.

Table 6 CPU recovery rates

Variable	Warm part	Cold part	Global
Recovery rate (%)	100	53	53

It is important to highlight that the unit was designed to achieve >70 % of recovery rate but considering that the CO_2 composition in the inlet of the unit had to be 70 % v w/b (much higher in comparison with the 62 % v w/b presented in the table 3). With this, it is clear that the recovery rate depends clearly on the CO_2 composition in the inlet of the unit being the main contaminants moisture, nitrogen (depends on the false air or infiltrations across the depuration train) and oxygen (depends on the boiler excess and the infiltrations). If we considering the recovery rate obtained in the warm part, we may note that moisture is not affecting the process i.e. the flue gas condenser and the dryers are designed to deal with these moisture values, concluding that the incondensable gases will be the most important contaminants.

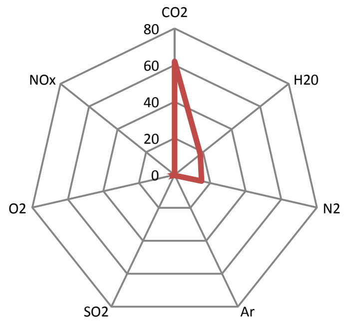


Fig. 10 Main impurities in the flue gases inlet stream.

4. Conclusions

This paper describes the unit designed by Air Liquide and installed in CIUDEN with a high degree of detail, their sub-units in which the CO_2 composition is increased to achieve the design value of 99,0 % v in the liquefied product stream.

In addition, a case study based on an empirical mass balance is included; considering this data, apart from the CO_2 purity, the mass balance also provides the recovery rate values, this parameter almost 100 % in the warm part of the unit whereas it is around 60 % in the cold part of the unit. Studying the specific behaviour of each subunit, it is important to highlight that the CO_2 composition at the CPU inlet was lower than 70 % v w/b, value that the unit was designed for.

As a next step, it was studied how to optimise the composition of flue gases in the CPU inlet stream, knowing that the main contaminants were, in this order, moisture, nitrogen and oxygen. Considering the first one, there were no problems to point out, i.e. the condenser and the flue gas dryers removed the moisture as expected. Therefore, H_2O is not a candidate for future optimisation. Regarding the second contaminant (nitrogen), it is dependent on the system infiltrations, i.e. the degree of tightness of the global installation (flue gas purification and CPU). Greater than expected N_2 levels caused the CO_2 recovery to be lower than expected. Therefore, it was concluded that system tightness is an important parameter in order to optimise CO_2 recovery rates. Finally, regarding the value of oxygen, it is necessary to maintain a specific excess of oxygen in the boiler outlet. Nevertheless in order to optimise the oxycombustion process, it is preferable to decrease it as much as possible and reduce the volume of flue gas that must be compressed always keeping in mind the security and the safety of the plant.

Considering these results, the conclusions are very clear on the necessity of increasing the quantity of experimentation hours on large pilot plants such as CIUDEN in order to further optimise the technology and reduce CAPEX uncertainty with the overall target of improving the business case for CCS.

Acknowledgements

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